

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



28

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 22/12, 22/17		A1	(11) International Publication Number: WO 97/13888 (43) International Publication Date: 17 April 1997 (17.04.97)
(21) International Application Number: PCT/US96/16740 (22) International Filing Date: 9 October 1996 (09.10.96) (30) Priority Data: 60/005,027 10 October 1995 (10.10.95) US 60/005,028 10 October 1995 (10.10.95) US (71) Applicant: COURTAULDS AEROSPACE, INC. [US/US]; 2820 Empire Avenue, Burbank, CA 91504 (US). (72) Inventors: AKLIAN, Jak ; 6551 Gentry Avenue, North Hollywood, CA 91606 (US). LEWIS, Kathrine, J. ; 11 Concho Lane, Canoga Park, CA 91307 (US). (74) Agents: SPRINKLE, Douglas, W. et al. ; Suite 400, 280 N. Woodward, Birmingham, MI 48009 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: NON-CHROMATE CORROSION INHIBITORS FOR ALUMINUM ALLOYS			
(57) Abstract A non-chromate, corrosion-inhibiting coating composition for metal surfaces includes at least one inhibitor selected from the group consisting of phosphates, phosphosilicates, silicates, and mixtures thereof, at least one inhibitor selected from the group consisting of titanates, zinc salts, and mixtures thereof, and a carrier for these inhibitors, the carrier capable of placing the inhibitors in proximity with the metal surface. In a preferred embodiment, the coating composition further includes a borate such as boric acid, and a succinate. A preferred phosphate includes calcium dihydrogen phosphate, and sodium titanium oxide is a preferred titanate. The zinc salt can include zinc phosphate or zinc cyanamide.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

-1-

**NON-CHROMATE CORROSION
INHIBITORS FOR ALUMINUM ALLOYS**

This application claims the benefit of U.S. Provisional Applications Nos. 60/005,027 and 60/005,028 filed October 10, 1995.

5

Field of the Invention

This invention relates generally to methods and compositions for inhibiting corrosion, and in particular, to methods and compositions for inhibiting corrosion of metals, especially aluminum and other light metal alloys used in aircraft. Most specifically, the present invention relates to a non-chromate containing, corrosion-inhibiting coating composition capable of protecting a wide variety of metal surfaces.

Background of the Invention

The U.S. Environmental Protection Agency has identified the metal finishing industry as one of the one most significant contributors to environmental pollution in the United States and, in all likelihood, throughout the rest of the world. This is because the materials currently most used in metal finishing include chromium, cadmium, zinc, lead, copper, nickel, chromates, and many toxic or polluting volatile organics.

The aircraft industry, being one of the largest of the industrial finishers, provides an example of the environmental impact of these processes. In a 1990 report, Tinker Air Force Base (Oklahoma) reported producing and treating 1.4 million gallons of industrial waste water per day mostly from metal finishing. The principal contaminants were chromium, nickel, copper, cadmium, lead,

-2-

zinc, tartrates, EDTA, phosphate, and ammonia. It is estimated that the cost of disposing of these wastes is approximately \$220 per ton, which equates to several thousand dollars per day for this one site.

5 The chromate ion, which is an excellent corrosion inhibitor, has been one of the most widely used for almost a hundred years. It is generally used as a pigment in corrosion inhibitive paints, wash primers, sealants and caulks. It is also used in chromate conversion coatings, etching solutions, and in sealing anodized and phosphate coatings.

10 For the past ten years, however, chromate has been recognized as toxic and carcinogenic, and because of its health risks, has become highly regulated. With pressure for elimination being exerted by government regulations, continued use of chromate will incur ever increasing economic penalties. Hence, there is urgent need for non-toxic substitutes, both from economic and environmental standpoints.

15 Currently, the most widely used inhibitors for passivating aerospace aluminum alloys and other light metals are the alkaline earth and zinc salts of hexavalent chromium. They vary mostly in their degree of water solubility (in the order $Mg > Ca > Sr \geq Zn$) and to a much smaller extent in their pH ($Sr \geq Ca > Mg$). The chromate anion is the active species, reliably performing
20 four necessary functions to be more fully described below. In addition, all of the above-described hexavalent chromium salts enhance adhesion in many paint and sealing systems.

-3-

Chromate performs four functions, thereby making it a desirable inhibitor. These functions include:

1. Rapid exit from a carrier matrix, such as paint or sealant.
2. Adsorption of the chromate anion on the bare metal or metal
oxide. This alters space charge distributions at the interface,
lowering the isoelectric point of the protective anodic metal oxide
layer naturally forming on active metals. This repels chloride
attack, and/or shifts the corrosion potential of that metal and/or
its pitting potential in the noble direction.
3. Instead of oxygen reduction at cathode sites, reduction of
chromium (VI) anion occurs to form an acid-insoluble
("persisting"), chromium (III) oxide layer at cathode sites. This
fills oxide voids over cathode sites and blocks further corrosion
reaction.
4. Buffering the pH or neutralizing increasing acidity at metal/
electrolyte interface which comes from metal oxidization in the
absence of air. Increasing acidity accelerates corrosion
exponentially.

In addition to these desirable inhibitive functions, chromate salts have the advantages of: (1) promoting adhesion at the metal/resin interface under a coating or sealant compound; (2) working well on a wide variety of metal and alloy substrates because they passivate both anodically and cathodically; (3)

-4-

being relatively neutral in pH; and (4) being strong oxidizers only in acid conditions, and thus not destroying or strongly reacting with the resin matrix in which they are placed.

The prior art discloses a number of non-chromate species which have some inhibitive capabilities. For example, U.S. Patent 5,126,074 discloses "hydrogen phosphate" anions as exhibiting corrosion inhibitive activity on aluminum. The patent further discloses the use in coatings of alkaline earth monohydrogen phosphates, together with a carbonate of the same alkaline earth metal and an additive of alkaline fluorosilicate or fluoroborate or alkali or alkaline fluoride. This combination is said to prevent filiform corrosion on aerospace aluminum alloys.

Other references cite the dihydrogen phosphate anion as adsorbing on alumina and lowering its isoelectric point (IEP) from pH=9 to pH=5. Lowering the IEP of aluminum oxide on aluminum metal has been shown to increase its resistance to pitting. Since this species also exhibits buffering capability, it performs functions 2 and 4.

U.S. Patent 2,624,708 discloses carcinogenic mercaptobenzothiazole (MBT) as an inhibitor for aluminum and steel. Sulphur and mercapto groups which are "soft bases" are known to have a high affinity for noble and other bare metal ("soft acid") surfaces. They are effective inhibitor structures under acidic conditions where no oxide is present. By itself, this species performs only function 2.

-5-

U.S. Patents 4,457,790 and 5,125,989 disclose the use of Mannich adducts of vegetable tannin or polyalkenyl phenols to "conversion coat" aluminum. A titanium ion or compound such as fluorotitanic acid, among others, is claimed as a co-reactant. U.S. Patent 5,129,967 discloses minute
5 catalytic amounts of dihydrohexafluorotitanic acid and hydrofluoric acid used with much larger amounts of dihydrohexafluorozirconic acid and polyacrylic acid. These patents refer to usages on aluminum and/or aluminum alloys.

U.S. Patent 5,314,532 discloses zinc, cobalt, nickel and lead cyanamide pigments as exhibiting corrosion inhibitive effects on silver and thin mirror
10 coatings. Bare, oxide-free copper would be expected to show adsorption characteristics somewhat analogous to silver, especially in an acidic, crevice environment. As with silver groups, the availability of electrons on the cyano group act as a "soft base" on bare metal "soft acid" surfaces, performing function
2.

15 The present invention provides a corrosion-inhibiting coating composition which performs many, if not all of the same functions as a chromate-containing composition, but without the need for the harmful chromate species. The problem solved by this invention is the elimination of toxic hexavalent chromium salts which are known to be human carcinogens, as
20 corrosion inhibitors from treatment solutions, coatings, and sealants used on aluminum and other metal alloys. The present invention provides for the synergistic combinations of non-chromate inhibitors for aerospace aluminum

-6-

alloys and other metal surfaces which can be incorporated into both curable and non-curing sealants and into curable primer and unicon systems. This synergistic combination of inhibitors can also be incorporated into water-containing or water-absorbing fluids that might cause corrosion when used in the proximity of metal such as de-icing liquids and coolants. These and other advantages of the present invention will be readily apparent from the description, discussion and examples which follow.

Summary of the Invention

There is disclosed herein a non-chromate, corrosion-inhibiting coating composition for metal surfaces. As used herein, "coating" is used to mean any composition which can cover a substrate, or which can place the inhibitors in proximity with a substrate. The composition comprises at least one inhibitor selected from the group consisting of phosphates, phosphosilicates, silicates, and mixtures thereof, at least one inhibitor selected from the group consisting of titanates, zinc salts, and mixtures thereof, and a carrier for these inhibitors, the carrier being capable of placing the inhibitors in proximity with the metal surface.

In particular embodiments, the coating composition of the present invention can further comprise a borate, such as boric acid, and/or a sulfur-containing succinate such as (2-benzothiazolylthio)succinic acid or amine salts thereof. A preferred phosphate is calcium dihydrogen phosphate. A preferred phosphosilicate is calcium, strontium zinc phosphosilicate. Sodium titanium

-7-

oxide is a preferred titanate. Zinc phosphate and/or zinc cyanamide are the preferred zinc salts. The carrier comprises a solution or polymer matrix which adheres well to metal substrates and is capable of placing the inhibitors in close proximity with the metal surface. The coating composition of the present invention may also include ancillary ingredients such as pigments, rheological agents, and other performance additives.

Detailed Description of the Invention

The present invention is directed to the synergistic combinations of two to six individual corrosion inhibitors contributing two to five separate functions to the inhibition of corrosion on metals. The coating composition is particularly well suited for protecting light metal alloys, such as the aluminum alloys used in aircraft.

In the broadest sense, the present invention comprises at least one inhibitor selected from the group consisting of phosphates, phosphosilicates, silicates, and mixtures thereof, at least one inhibitor selected from the group consisting of titanates, zinc salts, and mixtures thereof, and a carrier for the inhibitors, the carrier capable of placing the inhibitors in proximity with a metal surface. The coating composition of the present invention can further comprise a borate, such as boric acid, and/or a succinate, preferably a sulfur-containing succinate. The succinate comprises a compound selected from the group consisting of (2-benzothiazolylthio)succinic acid, the fatty amine salt of (2-benzothiazolylthio)succinic acid, and mixtures thereof. In a preferred

-8-

embodiment, the inhibitors are loaded into the carrier to achieve 3-40% by volume in a dried film, more preferably 5-25% by volume in a dried film, and most preferably 10-20% by volume in a dried film.

In a preferred embodiment, the phosphate comprises a dihydrogen phosphate, most preferably a compound selected from the group consisting of calcium dihydrogen phosphate, potassium dihydrogen phosphate, ammonium dihydrogen phosphate, sodium dihydrogen phosphate and mixtures thereof. The phosphate can also comprise a pyrophosphate, preferably sodium pyrophosphate, or a monohydrogen phosphate, preferably dipotassium monohydrogen phosphate.

The phosphosilicate of the present invention preferably comprises a compound selected from the group consisting of calcium, strontium phosphosilicate, calcium, strontium, zinc phosphosilicate, and mixtures thereof. The silicate of the present invention preferably comprises an orthosilicate, most preferably tetrasodium orthosilicate.

In a preferred embodiment of the present invention, the titanate comprises a titanium oxide, more preferably sodium titanium oxide. The zinc salt preferably comprises a compound selected from the group consisting of zinc phosphate, zinc cyanamide, and mixtures thereof.

When used in the coating composition of the present invention, boric acid should be loaded into the carrier so that it occupies up to 10% by volume in a dried film, more preferably 0.3-5.0% by volume in a dried film, and most

-9-

preferably 0.5-2% by volume in a dried film. Likewise, when used as an inhibitor, calcium dihydrogen phosphate can be added in an amount up to 10% by volume in a dried film, more preferably 0.3-7% by volume, and most preferably 0.5-5% by volume in a dried film. When calcium, strontium phosphosilicate or calcium, strontium, zinc phosphosilicate is used as an inhibitor, it can be added in an amount up to 25% by volume in a dried film, more preferably 0.3-10% by volume, and most preferably 1-5% by volume in a dried film. If (2-benzothiazolylthio)succinic acid or the fatty amine salt of (2-benzothiazolylthio)succinic acid is used as an inhibitor in the coating composition of the present invention, it can be loaded into the carrier in an amount up to 10% by volume in a dried film, more preferably 0.3-5% by volume, and most preferably 0.5-3% by volume in a dried film. Sodium titanium oxide can be added in an amount up to 10% by volume in a dried film, more preferably 1-10% by volume, and most preferably 3-6% by volume in a dried film. Zinc phosphate or zinc cyanamide, when used in the present invention can be added in an amount up to 15% by volume in a dried film, more preferably 1-10% by volume in a dried film, and most preferably 3-6% by volume.

The carrier of the present invention is any compound which is capable of adhesion to a metal surface, and is also capable of placing the combination of inhibitors in proximity with the metal surface. Suitable carriers include both curable and noncuring sealants, as well as curable primer and unicon systems.

-10-

The combination of inhibitors of the present invention can also be incorporated into water-containing or water-absorbing fluids that might cause corrosion when used in the proximity of metal such as de-icing liquids and coolants which are primarily comprised of glycol and water. Other carriers include, but are not limited to, aqueous solutions, amine-cured epoxy coatings, polyester and urethane coatings, sealant matrices such as those based on epoxy-cured polythioether polymers, MnO_2 cured polysulfide sealants, non-curing end-capped polysulfide sealants, and other carriers as are known in the art.

Additional materials can be added to the coating composition of the present invention such as pigments, rheological agents, adhesion promoters and other additives, as are known in the art. For example, an oily, hydrophobic additive can be used with some of the inhibitor combinations of the present invention to achieve more acceptable barrier performance of sealants in water. Additionally, since the inhibitor ingredients of this invention do not necessarily enhance adhesion as do oxidizing inhibitors such as chromate, a porous conversion coating or anodized layer on the substrate is required in very wet environments for good mechanical adhesion of a coating or sealant to the metal.

As has been discussed above, chromate has been identified as an excellent inhibitor because it performs the following four necessary functions:

1. Rapid polymer exit and short term metal passivation.
2. Passivation by metal surface adsorption and double layer space charge altering.

-11-

3. Forming a water insoluble passivation layer which persists or remains insoluble in neutral, alkaline and acidic environments.
4. Passivation by control of pH or neutralization of acid at the metal/ electrolyte interface.

5 Therefore, in order to replace chromate, any combination of inhibitors must perform at least some, if not all of these functions in order to operate as a successful corrosion inhibitor. Additionally, transport of itself and other inhibitors out of a solid, e.g. polymeric, carrier matrix onto adjacent exposed bare metal areas in a moist but not liquid immersed environment is a performance parameter exhibited by one of the inhibitors (boric acid) of this invention that is not exhibited by chromate.

In general, the first and second inhibitive functions are performed by one or more moderately water-soluble, fast but reversibly adsorbing ingredients which exit readily from a coating or sealant, to give rapid, short-term passivation of a metal surface. Boric acid appears to have the predominant fast or first-response effect out of a polymer matrix, and appears to also aid in releasing other, less soluble, more permanent passivators from the polymer.

The third inhibitive function is performed by a slower responding combination of two ingredients to form a water-insoluble, acid-resistant, "persisting" passivation layer. By "persisting" is meant remaining on a metal surface that was exposed to inhibitor-containing solution after that inhibitor-containing solution is removed and replaced with a corrosive solution such as

-12-

aqueous sodium chloride containing no inhibitor. This layer is believed to form on the bare metal as well as on the oxide. The combination of zinc phosphate or zinc cyanamide and (2-benzothiazolylthio)succinic acid or its fatty amine salt perform this function.

5 The fourth inhibitive function of these systems consists of buffering the pH, or controlling (neutralizing) the acidification of the metal-electrolyte interface environment in anaerobic or crevice conditions. Acid conditions dissolve the protective oxide and do not allow new insoluble oxide to form. In the formulations described by the present invention, dihydrogen phosphates, 10 monohydrogen phosphates, pyrophosphate, orthosilicate, titanate, phosphosilicates and cyanamide can perform this function.

A variety of different quantitative and qualitative test methods have been employed to identify and corroborate passivation behavior on aircraft aluminum. These include:

- 15 1. Galvanic Current Measurement (on solutions, coatings and sealants)
- a. Uses a titanium cathode electrically shorted to the active metal, usually Al alloy, immersed in aqueous NaCl solution. Stainless steel, Cd plated steel and carbon 20 composite cathodes are also used.

-13-

- 5 b. Current between anode and cathode (Al and Ti or other, respectively) is measured at regular intervals and plotted versus time.
- c. Configuration accelerates development of acidic crevice conditions in a narrow, air-deficient gap between the parallel, spaced-off anode and cathode metals.
- 10 d. Used to quantitatively test functions 1, 2 and/or 4.
- e. We define good performance as 2-5 times the initial (i.e., within 24 hours) galvanic current reduction compared to uninhibited systems, with no rise over time out to 5-6 weeks. (Uninhibited coating and sealant initial currents are approximately 0.5-1 microamps per square centimeter on bare 2024 alloy with a Ti cathode, with a visual rise in current of 2-5 times within 1-2 weeks. Chromate gives
- 15 approximately 0.2-0.3 microamps per square centimeter initially, with no rise over time. The corresponding values are approximately 3-5 times higher for bare 7075 alloy with a Ti cathode.)
2. Electrochemical Impedance Spectroscopy (EIS) (on solutions,
- 20 coatings and sealants)
- a. Uses an active metal (e.g. Al alloy) working electrode, passivated stainless steel counterelectrode, calomel

-14-

reference electrode and Schlumberger potentiostat and frequency response analyzer.

b. Run in one or more of the following configurations:

i. Neutral or pH-adjusted, aerated NaCl solution, containing inhibitor(s).

ii. Active working electrode covered with inhibitor-containing, bonded coating or sealant film exposed to open, aerated NaCl solution on the upper film side. Measures barrier properties or corrosive-environment-penetration resistance (R_{pore}) of bonded films.

iii. Active working electrode covered with inhibitor-containing, non-bonded, "free film" of coating or sealant, exposed to open, aerated aqueous NaCl solution on the upper side. In this configuration, when the film is penetrated with liquid, the whole air-deficient electrolyte/active metal interface area is wetted and therefore known dimensionally to calculate accurate charge transfer resistances (R_{ct}).

c. Used quantitatively to test functions 2, 3 and/or 4.

d. We define good electrochemical performance as R_{ct} 's of greater than 10^6 ohm-square centimeters, persisting over

-15-

time. We define good barrier performance as exhibiting high (greater than 10^8 ohm-square centimeters), essentially immeasurable R_{pore} 's for as long as possible. We judge by making comparisons at equal film thicknesses. Low R_{pore} can be compensated for to a great extent by high R_{ct} as is the case with chromate.

3. Filiform Testing (on coatings only)

- a. Uses brief (usually one hour) HCl vapor exposure to initiate acidic filiform (underfilm crevice) corrosion conditions at cut edges of coatings. Subsequent 80+ % humidity exposure propagates further filiform corrosion.
- b. Relative effectiveness of inhibitors are compared on the same substrates. [Differences in corrosiveness of Al substrates (various alloys, Alclad, conversion-coated) usually give more variation for a given coating than the differences between inhibitors, including none, in the same coating, on the same substrate.]
- c. Use to qualitatively test function 4 and combined effects of functions 1-3.
- d. Good performance for a coating or coated system is usually defined as the development from a cut edge of filiforms no greater than 3-6 millimeters in length, with

-16-

the majority less than 3 millimeters, after 1000 or more hours.

4. Salt Spray Testing (on coatings and sealants)

5 a. Uses condensing corrosive (5%) salt solution to cause electrochemical activity of soluble inhibitors to be a factor, along with barrier properties, but the effects cannot be separately determined.

10 b. By leaving some uncoated area exposed, ability of inhibitors to move from the resin matrix to uncovered or damaged areas and to protect them is determined.

c. As in filiform testing, relative effectiveness of inhibitors are compared on the same substrates.

d. Used to qualitatively test function 1 and combined effects of functions 2-4.

15 e. Good performance is usually defined as no corrosion blister formation away from cut edges and minimal undercutting or corrosion blister formation at cut edges. Judgments are usually based on visual comparisons over time with uninhibited and chromate-inhibited controls.

20 5. pH Range Immersion Testing (on solutions only - solutions containing inhibitors, buffered from pH 3-10)

-17-

- a. Found to be a predictor of "persisting" (insoluble) passivation layer formation and of resistance to prolonged-exposure, acidic-condition crevice corrosion.
- b. Used to test function 3.
- 5 c. We define good performance as resistance to visual corrosion on flat surfaces and cut edges of bare metal over a wide pH range for as long as possible; on more than one alloy, if possible. Judgments are based on visual comparisons over time with uninhibited and
10 chromate inhibited controls.

In order to work at all, effective inhibitors must exhibit at least function 2, corrosion current suppression. Functions 1, 3 and 4 increase their effectiveness. In addition, whether they perform on one or both of the most common aerospace aluminum substrates (AA2024-T3 or AA7075-T6) (function
15 5), and whether their addition significantly lowers the water resistance/adhesion of a polymer matrix (function 6) is considered.

The following table summarizes some of the preferred inhibitor combinations, rated according to how many of the above six functions they perform. This invention, however, is not limited to the combinations below.
20 These abbreviations have been used to identify the various inhibitors in which:

B = boric acid

C = calcium dihydrogen phosphate

-18-

K = dipotassium monohydrogen phosphate

A = ammonium dihydrogen phosphate

P = sodium pyrophosphate

5 H = calcium, strontium phosphosilicate or calcium,
strontium, zinc phosphosilicate

S = tetrasodium orthosilicate

I = (2-benzothiazolylthio)succinic acid or the fatty
amine salt of (2-benzothiazolylthio)succinic acid

N = sodium titanium oxide

10 Z = zinc phosphate

W = zinc cyanamide

PREFERRED INHIBITOR COMBINATIONS					
GOOD (1-2 functions)		BETTER (3-4 functions)		BEST (5 functions)	
Inhibitor	Function	Inhibitor	Function	Inhibitor	Function
15 CN	2,5	BINZ	1,2,3,5	BCINZ	1,2,3,4,5
KI	2,5	BCNZ	1,2,4,5	BCINW	1,2,3,4,5
PS	2,4	BNZ	1,2,5	HINZ	2,3,4,5,6
		IZ	2,3,6	CINZ	2,3,4,5,6
		INZ	2,3,6		
20		HN	2,5,6	SrCrO ₄	2,3,4,5,6
		HINS	2,4,5		
25 Functions = 1 = exposed metal passivation adjacent to polymer 2 = low galvanic current, high EIS R _{ct} 3 = formation of "persisting layer" 4 = crevice condition low galvanic current 5 = performs on both 2024 and 7075 alloys 6 = good water swell resistance (low water solubility)					

-19-

The present invention will best be illustrated by the following tables of examples. The same inhibitor abbreviations set forth above have also been used in these tables. A series of compositions were prepared and tested on several light metal alloys. The test samples were prepared according to the tables set forth below, all components being mixed together in a vessel, and the various formulations were applied to 2024 and 7075 alloy substrates. The samples were run through a series of tests to test their corrosion-inhibitive properties. These tests have already been discussed, with the results summarized above. In the examples, as in the rest of the specification and claims, all percentages are by volume in a dried film.

FORMULATIONS (as volume % of non-volatiles)

Components	Non-curing Sealants		Cured Sealants		Solvent-borne Primer Coatings		
	HINZ	BCINZ	BCINZ	CINZ	BCINZ	BCNZ	BCINW
Non-curing polysulfide resin	71.1	69.9	-	-	-	-	-
Epoxy-cured polythioether resin	-	-	73.7	73.6	-	-	-
Amine-cured epoxy resin	-	-	-	-	64.0	64.0	75.2
Adhesion promoters, dispersants, flow agents	1.0	1.0	0.2	0.2	4.0	4.0	10.1
Inert fillers	21.8	21.3	9.0	9.0	13.4	14.8	2.3
H	1.2	-	-	-	-	-	-
B	-	2.2	2.2	-	2.9	2.9	1.4

-20-

5

	Non-curing Sealants		Cured Sealants		Solvent-borne Primer Coatings		
C	-	1.4	2.0	4.0	2.9	2.9	1.4
I	0.6	0.6	6.5	6.6	1.4	-	0.7
N	1.2	1.1	2.0	2.1	5.7	5.7	4.8
Z	3.1	2.5	4.4	4.5	5.7	5.7	-
W	-	-	-	-	-	-	4.1
Solvent	(+20)	(+20)	(+10)	(+10)	(+70)	(+70)	(+320)
Water	-	-	-	-	-	-	-

10

15

20

25

Water-borne Primer Coatings						
Components	BCINZ	BCINW	BCNZW	BCNZ	BCNW	CINZ
Non-curing polysulfide resin	-	-	-	-	-	-
Epoxy-cured polythioether resin	-	-	-	-	-	-
Amine-cured epoxy resin	69.1	69.1	69.1	69.1	69.1	69.1
Adhesion promoters, dispersants, flow agents	1.7	1.7	1.7	1.7	1.7	1.7
Inert fillers	9.9	9.9	11.5	14.3	15.9	13.2
H	-	-	-	-	-	-
B	3.3	3.3	3.3	3.3	3.3	-
C	3.3	3.3	3.3	3.3	1.7	3.3
I	1.7	1.7	-	-	-	1.7
N	5.5	5.5	5.5	5.5	2.8	5.5
Z	5.5	-	2.8	2.8	-	5.5
W	-	5.5	2.8	-	5.5	-
Solvent	(+28)	(+28)	(+28)	(+28)	(+28)	(+28)
Water	(+200)	(+200)	(+200)	(+200)	(+200)	(+200)

-21-

It will be appreciated from the foregoing, that a non-chromate containing coating composition having excellent properties for inhibiting corrosion of a variety of metal surfaces may be prepared from the synergistic combination of two to six individual corrosion inhibitors contributing two to five separate functions to the inhibition of metals, such as light metal alloys. The specific components of the composition will depend upon particular applications and factors such as the metal alloy substrate, the particular polymer or solution matrix in which the inhibitors are carried, and the range of exposure conditions the material will see in its particular location (e.g. aircraft interior, exterior, fuel tank, skin coating, lap seam, etc.).

The foregoing discussion and examples are merely meant to illustrate particular embodiments of the invention, and are not meant to be limitations upon the practice thereof. It is the following claims, including all equivalents, which define the scope of the invention.

We claim:

-22-

CLAIMS

1 1. A non-chromate, corrosion-inhibiting coating composition for
2 metal surfaces, said composition comprising:

3 at least one inhibitor selected from the group consisting of
4 phosphates, phosphosilicates, silicates, and mixtures thereof;

5 at least one inhibitor selected from the group consisting of
6 titanates, zinc salts, and mixtures thereof; and

7 a carrier for said inhibitors, said carrier capable of placing said
8 inhibitors in proximity with said metal surface.

1 2. The coating composition of claim 1 and further comprising a
2 borate.

1 3. The coating composition of claim 2 wherein said borate comprises
2 boric acid.

1 4. The coating composition of claim 3 wherein said boric acid
2 comprises up to 10 percent by volume in a dried film.

1 5. The coating composition of claim 1 and further comprising a
2 succinate.

-23-

1 6. The coating composition of claim 5 wherein said succinate
2 comprises a sulfur-containing succinate.

3 7. The coating composition of claim 6 wherein said succinate
4 comprises a compound selected from the group consisting of (2-
5 benzothiazolylthio)succinic acid, the fatty amine salt of (2-
6 benzothiazolylthio)succinic acid, and mixtures thereof.

1 8. The coating composition of claim 7 wherein said succinate
2 comprises up to 10 percent by volume in a dried film.

1 9. The coating composition of claim 1 wherein said phosphate
2 comprises a hydrogen phosphate.

1 10. The coating composition of claim 9 wherein said hydrogen
2 phosphate comprises a compound selected from the group consisting of calcium
3 dihydrogen phosphate, ammonium dihydrogen phosphate, sodium dihydrogen
4 phosphate, potassium dihydrogen phosphate and mixtures thereof.

1 11. The coating composition of claim 9 wherein said hydrogen
2 phosphate comprises dipotassium monohydrogen phosphate.

-24-

1 12. The coating composition of claim 9 wherein said hydrogen
2 phosphate comprises up to 10 percent by volume in a dried film.

1 13. The coating composition of claim 1 wherein said phosphate
2 comprises a pyrophosphate.

1 14. The coating composition of claim 13 wherein said pyrophosphate
2 comprises sodium pyrophosphate.

1 15. The coating composition of claim 1 wherein said phosphosilicate
2 comprises a compound selected from the group consisting of calcium, strontium
3 phosphosilicate; calcium, strontium, zinc phosphosilicate; and mixtures thereof.

1 16. The coating composition of claim 15 wherein said phosphosilicate
2 comprises up to 25 percent by volume in a dried film.

1 17. The coating composition of claim 1 wherein said silicate
2 comprises an orthosilicate.

1 18. The coating composition of claim 17 wherein said orthosilicate
2 comprises tetrasodium orthosilicate.

-25-

1 19. The coating composition of claim 1 wherein said titanate
2 comprises an alkaline titanium oxide.

1 20. The coating composition of claim 19 wherein said titanium oxide
2 comprises sodium titanium oxide.

1 21. The coating composition of claim 20 wherein said sodium
2 titanium oxide comprises up to 10 percent by volume in a dried film.

1 22. The coating composition of claim 1 wherein said zinc salt
2 comprises a compound selected from the group consisting of zinc phosphate,
3 zinc cyanamide, and mixtures thereof.

1 23. The coating composition of claim 22 wherein said zinc salt
2 comprises up to 15 percent by volume in a dried film.

1 24. A non-chromate, corrosion-inhibiting coating composition for
2 metal surfaces, said composition containing inhibitors, said inhibitors
3 comprising:

4 at least one compound selected from the group consisting of boric
5 acid; dipotassium monohydrogen phosphate; calcium dihydrogen phosphate;

-26-

6 ammonium dihydrogen phosphate; sodium dihydrogen phosphate, potassium
7 dihydrogen phosphate; sodium pyrophosphate; calcium, strontium
8 phosphosilicate; calcium, strontium, zinc phosphosilicate; tetrasodium
9 orthosilicate; and mixtures thereof;
10 sodium titanium oxide;
11 at least one compound selected from the group consisting of zinc
12 phosphate, zinc cyanamide, and mixtures thereof; and
13 a carrier for said inhibitors, said carrier capable of placing said
14 inhibitors in proximity with said metal surface.

1 25. The coating composition of claim 24 and further comprising at
2 least one compound selected from the group consisting of (2-
3 benzothiazolylthio)succinic acid, the fatty amine salt of (2-
4 benzothiazolylthio)succinic acid, and mixtures thereof.

1 26. The coating composition of claim 24 wherein said inhibitors
2 comprise 3-40 percent by volume in a dried film.

1 27. A non-chromate, corrosion-inhibiting coating composition for
2 metal surfaces, said composition containing inhibitors, said inhibitors
3 comprising:

-27-

4 at least one compound selected from the group consisting of boric
5 acid, calcium dihydrogen phosphate, and mixtures thereof; or

6 at least one compound selected from the group consisting of
7 calcium, strontium phosphosilicate; calcium, strontium, zinc phosphosilicate;
8 and mixtures thereof;

9 at least one compound selected from the group consisting of (2-
10 benzothiazolylthio)succinic acid, the fatty amine salt of (2-
11 benzothiazolylthio)succinic acid, and mixtures thereof;

12 sodium titanium oxide;

13 at least one compound selected from the group consisting of zinc
14 phosphate, zinc cyanamide, and mixtures thereof; and

15 a carrier for said inhibitors, said carrier capable of placing said
16 inhibitors in proximity with said metal surface.

1 28. The coating composition of claim 27 wherein said boric acid
2 comprises 0.3-10 percent by volume in a dried film.

1 29. The coating composition of claim 27 wherein said calcium
2 dihydrogen phosphate comprises 0.3-10 percent by volume in a dried film.

1 30. The coating composition of claim 27 wherein said phosphosilicate
2 comprises 0.3-25 percent by volume in a dried film.

-28-

1 31. The coating composition of claim 27 wherein said sulfur
2 containing succinate compound comprises 0.3-10 percent by volume in a dried
3 film.

1 32. The coating composition of claim 27 wherein said sodium
2 titanium oxide comprises 1-10 percent by volume in a dried film.

1 33. The coating composition of claim 27 wherein said zinc compound
2 comprises 1-15 percent by volume in a dried film.

1 34. A method for inhibiting corrosion on metal surfaces, said method
2 comprising contacting said metal surface with a coating composition comprising:
3 at least one inhibitor selected from the group consisting of
4 phosphates, phosphosilicates, silicates, and mixtures thereof;
5 at least one inhibitor selected from the group consisting of
6 titanates, zinc salts, and mixtures thereof; and
7 a carrier for said inhibitors, said carrier capable of placing said
8 inhibitors in proximity with said metal surface, said coating composition being
9 free of chromate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/16740

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C23C 22/12, 22/17

US CL : 148/247, 260, 271

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/247, 260, 271

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,110,129 (MATSUSHIMA ET AL) 29 August 1978, col. 3 line 5 to col. 4 line 6.	1-4,9-14,34
Y	US, A, 3,732,115 (LANKARD ET AL) 08 May 1973, col. 3, lines 25-75.	1,2, 17-21,34
Y	US, A, 4,145,462 (KUWABARA ET AL) 20 March 1979, col. 6, lines 55-60.	1,2,17,18, 34

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	g	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

11 FEBRUARY 1997

Date of mailing of the international search report

11 MAR 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SAM SILVERBERG

Telephone No. (703) 305-9646

THIS PAGE BLANK (USPTO)